Course on Stereochemistry
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Mod06 Lecture 25
Conformational Analysis of Substituted Cyclohexanes (Contd.)

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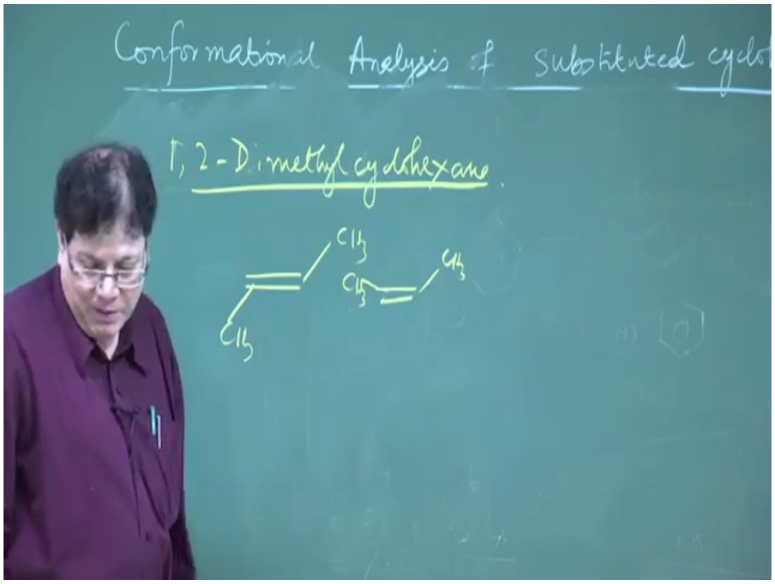

Okay now let us go to the cyclohexane disubstituted-cyclohexane where the substituents are in the 1,2 relationship okay and we will take the simplest case 1, 2-dimethyl cyclohexane, okay. Now what now here is said when you come to this 1, 2 system or 1, 3 system, there is this question of stereo isomerism, the real stereo iso not the conformational. The stereo isomerism which were classified as Diastereomers. So now you have a case of diastereomerism not the conformational diastereomerism, but the diastereomerism where the diastereomers cannot be inter-converted by rotation that situation arises here. How? Like what are diastereomers we know that like Cis and trans butane, they are diastereomers and they cannot be interconverted by rotation you have to break the bond and then make the bond to convert one from the other, okay. So they are diastereomers. These are called Cis and Trans.

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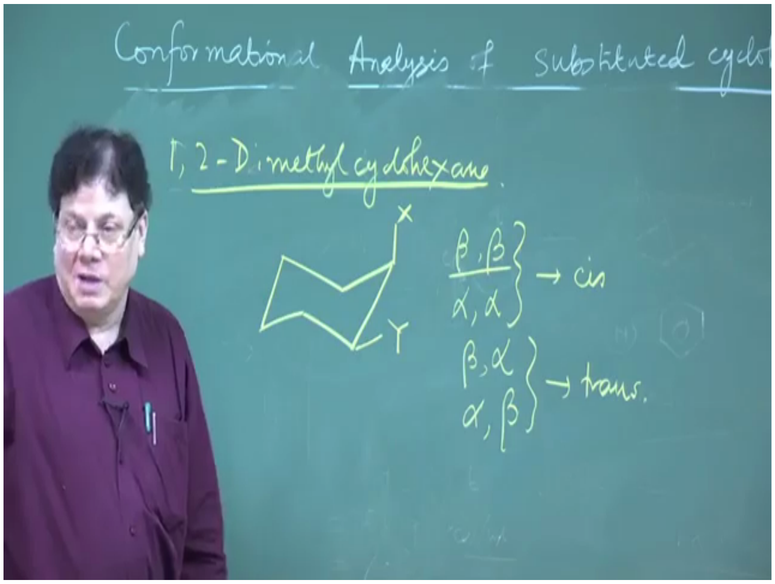

Similarly, in 1,3-disubstitited, 12 or it is 1,3 or 1,4 in disubstituted system not the 1,1 when it is 1,2, 1,3 and 1,4 what happens, because the substituents can have alpha or beta orientation, so you have different possibilities like if there are suppose an x group and then an y group, suppose the relationship between x and y not in terms of axial equatorial in terms of alpha beta, in this form you see both are beta. So if both the substituents occupy the same facial relationship means the both are beta or both are alpha then that is called a Cis isomer.

On the other hand if one substituent is beta another is alpha or vice versa that is called the trans isomer, okay. So that is a first step. So in 1, 2-dimethyl cyclohexane that can exist in Cis form or in the trans form, okay. So we have to separately consider these two forms.

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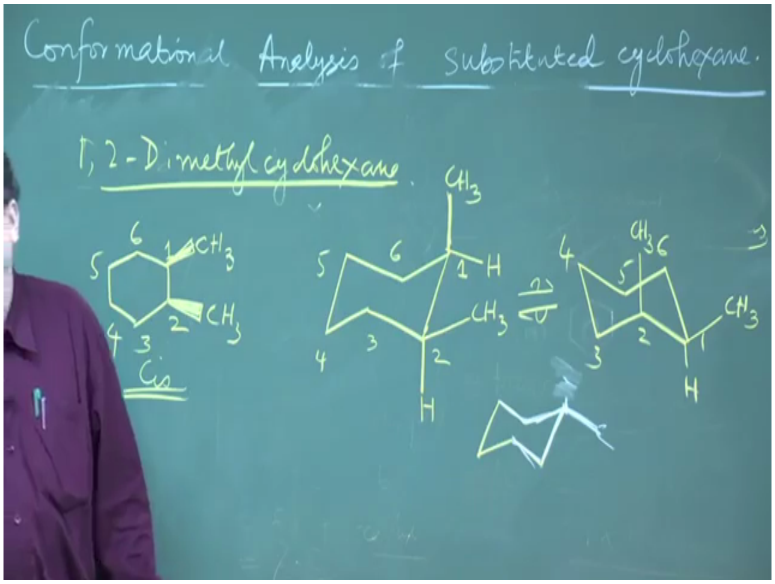

So first take the Cis form, okay. Now what is the Cis form in just be planar formula if I write it in this hexagonal formula. It is not having this type of conformation, but just for simplicity. Let us first draw the hexagon and what is the Cis compound that is Cis dimethyl cyclohexane, 1, 2-dimethyl cyclohexane. So if I put one methyl beta then I have to put the other methyl also in the beta orientation, oaky I could have done the opposite one. This could be alpha then that that be the alpha. So this is the Cis isomer, okay.

Now this is not the conformation, because this is the planar hexagon that is we know that it does not exist in the plane hexagon formula structure. So what it does we have to draw now a convert it the into the chair form. So convert it into the chair form, suppose this is your one carbon this is your two carbons 3,4,5,6. So suppose this is one this is 2, this is 3, 4, 5, 6. Now at 1 you have the methyl and which is beta. Now you know at one there are two substituents, one axial another is equatorial, but the e equatorial is in the alpha form and the axial is in the beta form. So this methyl has to be put in the axial orientation. So first you consider the alpha beta nature and the accordingly you place it in the axial or equatorial position.

So methyl will be equatorial and the hydrogen sorry methyl will be axial and the hydrogen will be equatorial at C1, at C2 you have to now place the you have two bonds equatorial and axial at C2 what will happen, because the methyl is beta, so we have to place it in this position and this is the hydrogen, so that is one conformation, okay. This conformation one methyl is axial another methyl is equatorial, oaky. So if you flip this molecule the energy will not be different at all, because again you have the similar situation one methyl will be axial and another methyl will be equatorial, remember in flipping axial becomes equatorial equatorial becomes axial but alpha remains alpha, beta remains beta.

So now in flipping this C1 you have brought down C4 you have brought up, so this is 4, this is 1, 1,2,3,4,5,6, so at C1 you have the methyl which was earlier axial now it will be equatorial and that C2 you have this beta equatorial, so now that will be beta axial, okay both have equal energy, because in both there is one axial methyl there is one equatorial methyl, but for suppose just for sake of problem if I ask that how much extra energy. Now this has over a cyclohexane chair, in a cyclohexane chair you have we have already calculated, that was 5.4 6 butane units and those 6 butane units where in the gauche form. So in this case if I ask that how much extra energy you have now incorporate into this system by putting these methyl groups in a Cis fashion, okay one axial another is equatorial. So what you have to do? You have to calculate again the number of butane units that you have incorporated by putting these (())(6:50) atoms okay.

Now what are the butane units? We know that if we attach one carbon to a cyclohexane you incorporate immediately two additional butane units, okay one is this another is this, we also know one more thing that if the substituents if the carbon is axial then these 2 butane units are in the gauche form and if the carbon is in the equatorial position then you introduce the butane units, but this butane units are in the anti. So equatorial carbon does not give any extra energy, okay.

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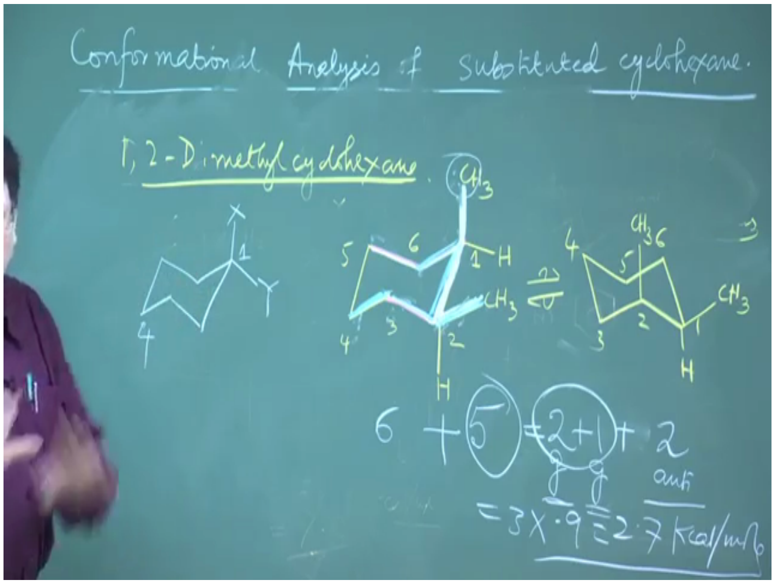

Now let us try to do that way that this is one carbon which you have attach to this C1 so what you have done? You have put you have incorporated two extra butane units one is this another is this okay and for this carbon you have introduced two extra butane units what are those? Those are this is the methyl, so one is this one another is this one okay, I can write it methyl 1, 6,5 methyl 1,2,3 that is for this carbon and then we have methyl 2,3,4 and then methyl 2,1,6 okay, but that is not the end of the story. There is one more extra thing that is there and that should not a escape our eye and that is, because this methyls are in the 1,2 position, so now they themselves form a butane units and that is this one white chock will show.

So an extra butane unit is there and that is because they are placed in a 1, 2 fashions. So number of extra butane units in this form is 6 is already there in the cyclohexane, but the xx (())(9:06) so 6 plus now the plus is, now you have 5 butane units, 2 for each carbon atom that we have introduced and another is the mutual butane unit from the butane unit form due to their mutual relationship by 1,2 relationship, so you have 5 butane units, but out of these 5 now we have to find out.

How many are gauche and how many are anti. So out of this 5, because this axial this is axial so a axial will introduce 2 gauche butane. So out of this 5 if you break down this five, so out of this two are from this axial methyl, they are in the gauche form and equatorial methyl does not introduce any extra energy, because they are in the anti-form. So this two are in the anti but the mutual one, this one is another gauche (())(10:06) okay. So two in the gauche unit one is in the gauche that is the mutual and the rest two are in the anti (())(10:17), I hope this is clear. So this does not these are the anti, these are the gauche and then the mutual one is also the gauche form. So the extra energy that you have is extra energy over a cyclohexane is 2 plus 1 that means 3 into 0.9, so 2.7 kilo calorie per mol okay. So that is clear.

Now this mutual relationship will not be there if they are in the 1, 3 position. This happens, because they are in the 1, 2 they are having a 1, 2 relationship okay. The next question that comes that is also very interesting that what is the is this (())(11:08) we have not describe the (())(11:10) here, because in 1,1 system there is no question of chirality (())(11:15), because when you have to different groups even if we have two different groups there will be a plane of symmetry going through this carbon and this 4 th carbon, C1-C4 will form a plane which is a plane of symmetry for this form.

So 1,1 will not be (())(11:31), but once you have this 1,2, 1,3 system then this (())(11:38) issue also come that whether this molecule is chiral (())(11:41) or not that is little bit tricky, because what happens how to check (())(11:48) of a molecule either you can see whether there is any symmetry present in a molecule or not that is one way. The other way you draw the mirror image and try to see whether this superimpose or not okay.

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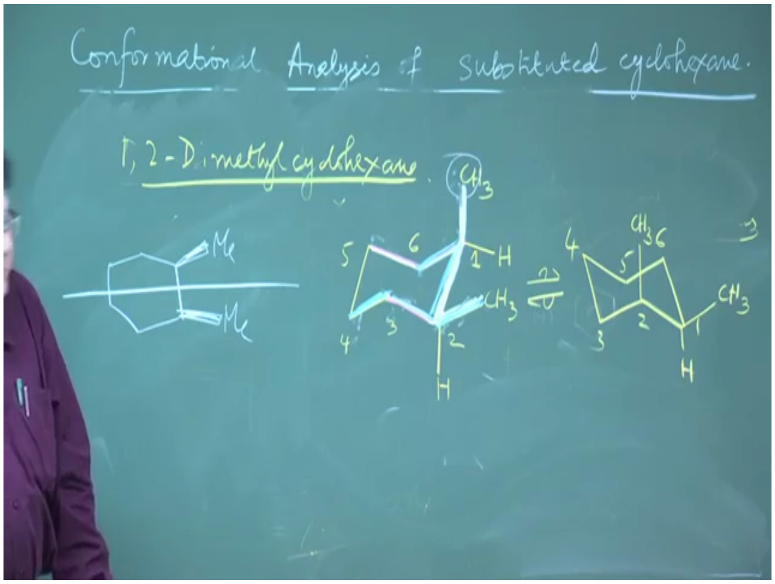

Now interestingly if you draw these molecule in the cyclohexane as a planar hexagon, you will immediately see that it appears that it has got a planar symmetry if you draw it in this fashion, but in the actual conformation, this is axial that is equatorial, so there is no planar symmetry. So in the actual means this is the conformer, so actual conformer does not have any plane of symmetry okay.

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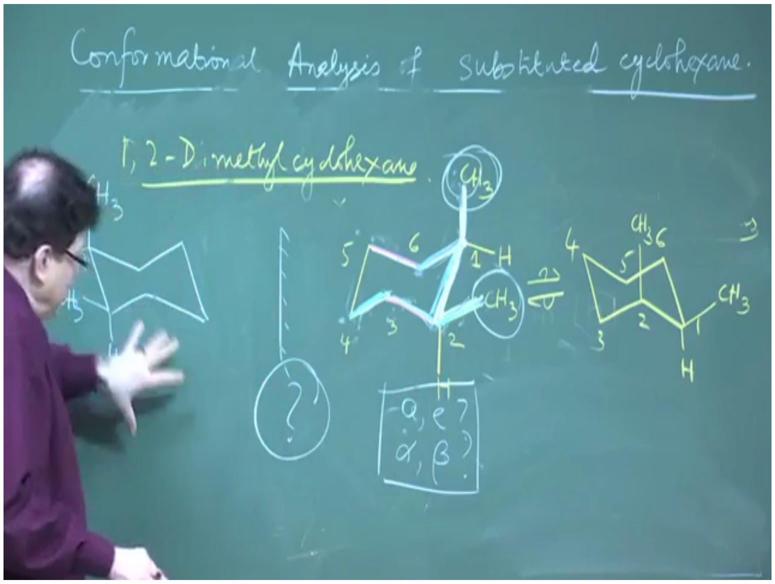

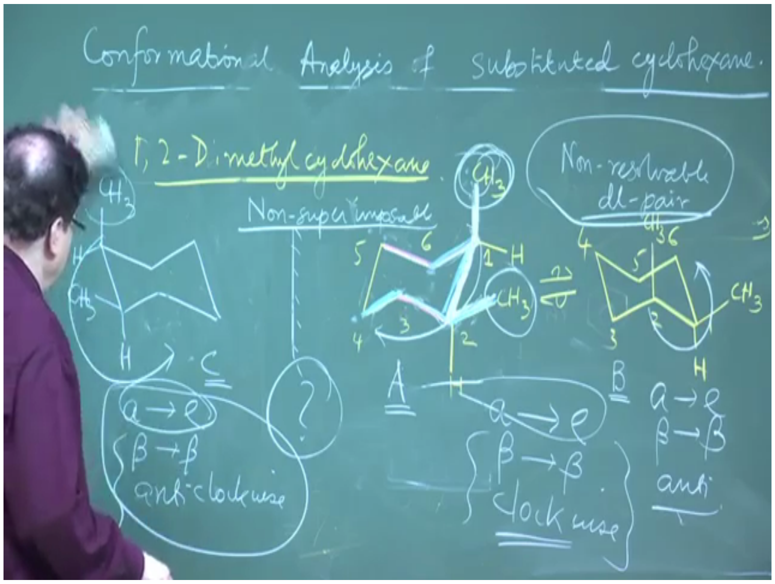

So the question is now there is a this planar symmetry is gone. So the question is now is it chiral? So how to answer that, so you draw the mirror image of this, because it will be difficult to inspect all sorts of symmetry element in this type of system, because you you may miss a symmetry element be doing so. So better draw the mirror image and if you draw the mirror image and then try to see whether they are same or not, okay. So what will happen? In the mirror image chair has to be the mirror image and then put that groups. So this methyl will be here and the other methyl will be on this side, okay. So this is the picture the mirror image. Now the question is are they superimposable? What is the relationship (())(13:32) are they superimposable or not.

Now this is this is how to answer this type of question that relationship between different chair forms, the same molecule writurn in different types of ways. So whether these are same or they are not same? How to decide on that okay. Now there are again different ways. Today I will give you a again a mnemonic device by which you can compare this verses this. The best way of comparing this and that is to try to turn it around, this is a problem is you cannot directly say whether these are to the same or not (())(14:16) the problem is on this lift side at the methyl and here on the right side at the methyl.

So either you now start rotating it and try to bring the methyls in the respective positions where which are here and then see whether they are same or not okay. Now that is one way may be next time I will do that, today I will give you just a mnemonic device. Mnemonic device is that will quickly solve this issue that whether they are same or not. That device depends see that relies on the relationship between these two methyls, so I can have different types of relationship between the methyl, I can check whether they are axial or equatorial? What is their status? I check whether they are alpha or beta that status I can check and thing I just incorporate that is that I decide to traverse through these carbon chains and come back to 1 that means I start walking from here go to C2, the minimum that is that the, because (I can) I could have gone the other way around also, but I want the carbon which is having the substituent to come very quickly.

So I start walking from C1 then come to C2 then C3 then C4 then C5 then C6 and come back to C1 (())(15:49) okay. So I do the this walking across the ring system in both the molecules okay and then see. So that means I have now 3 parameters, one is as I said axial equatorial nature of the subsequent, the other is the alpha-beta nature of the substituent and a 3rd parameter I am introducing that I am trying to go from 1 then 2 to 3, 3 to so I am I want to traverse through the ring in such a ways that the substituents come very quickly, because I could have gone again I repeat I could have gone this way or that way the first I go to un-substituted carbon then another un-substituted carbon then un-substituted then un-substituted then the substituted (())(16:32) rather than doing so what I do, I decided to walk in a such a way traverse in such a way that the substituted carbons come very quickly okay the shortest path in that (())(16:43).

So I have a directions see when I come from this to that and then traverse like this I have directionality now, because whether it is clockwise or anticlockwise. So if I have these 3 parameters and then write those parameters and then have the same 3 parameters here and then compare them okay, I an example will make it very clear, suppose I decide that I come from this axial I start from here that means I come from this axial methyl and go to the equatorial methyl, so this way 1 then 2 then 3 then 4 then 5 then 6.

So I fix this axial to equatorial motion. So I come from axial to equatorial, I could have done the other way (())(17:32), but suppose I fix it that I go from this axial methyl to the equatorial methyl and finally then C3 , C4, C5, C6. So how are they behaving means in terms of facial relationship, I am going from a beta methyl to a beta methyl okay. The beta methyl relationship and what is my direction if I do that I am actually traversing in a clockwise fashion, I am traversing in a clockwise fashion okay. So the direction is clockwise rotation okay, I do the same thing here okay, but I fix the first one I do not change the first one axial to equatorial.

So if I want to move from an axial methyl to equatorial methyl, I have to start from this position and then come back to the equatorial methyl and I see these 3 parameters. So axial to equatorial (())(18:36) and then I see that what is the facial relationship? This is beta and this is also beta. So in the first two are same, so what is different is that I now traverse in an anticlockwise direction okay.

Now out of these 3 this will always be the same, because that is the first parameter I fixed I do not change that parameter axial to equatorial that parameter I fix. So that is fixed then I compare this two, I compare these two if I see that there is one difference there, there is only one difference anticlockwise that is clockwise, then these two are not same. They are mirror images of each other and if I see that both are or these two are same that means all three are same then they are same molecules okay and if I see that these two are both different, see there are 3 same arrows, because this I have already fixed the axial-equatorial.

So I have two more parameters if both the parameters are same then the molecules are same. If one of the parameter is different than they are mirror images of each other. If both the parameters are different then again it comeback to the original situation that means both the molecules are same, see both are different then both the molecules are same. So these types of 3 seen arrows can come.

Here we are seeing only one difference. This is anti-clockwise that is clockwise. So they are not superimposing each other, they are different, they are non-superimposable. So according to the definition of chirality this molecule is that, because it shows the mirror image which is not same rotation (())(20:41). So this molecule is chiral, but nobody is (())(20:44) separate these two molecules why, because when you flip this molecule, see we have just check the relationship between the mirror image and the original image.

Now the question is when you flip this what happens whether this remains same with this or this becomes same with the mirror image or not. So we have to again put these 3 parameters and check. So I start from an axial to equatorial methyl that journey axial to equatorial and then it is beta to beta and this is the direction is again anti-clockwise.

So basically what is happening now (())(21:31). This is suppose my original A, this is my flipped form B and this is the mirror image C, okay I know that this should be chiral, because the mirror image is different, but however there is a problem. Now the flipped form becomes same as the mirror image, so if the flipped form becomes same as the mirror image and since both these two have same energy, because one axial one is equatorial situation. So in a mixture if you try to isolate this molecule half of this will flip and go into the mirror image that means this molecule will always exist as a 50-50 mixture of the two forms, the mirror image and the original image. Why they are remaining 50-50, because they have the same energy and they are obtain they are inter-convertible by flip. So this is what is called now non-resolvable a case of what is called a non-resolvable dl-pair. So if someone asks that what is the if A Cis 1,2-dimethyl cyclohexane chiral A Cis chiral (())(22:57) defiantly, because according to the definition of chirality mirror image is are not same okay, but you cannot separate these two, because by flipping this is converted to this form okay, that I have already shown by this mnemonic devices.

Uh next time I will do the rotation that by rotation how can you really prof that by that means the other way around I can say that when I flip this, it goes into the mirror image when I flip this molecule it goes into the mirror image, because the mirror image has been put to the identical with this molecule. So do not get confused again I can simplify a little bit. This is the original molecule if I flip it the flipped form is the mirror image at this point okay. So I do not have to draw the extra the mirror image. This is the mirror image and these two are present in 50-50 mixture and this as, because they have the same energy and energy barrier is very low, so it is you cannot separate these into individual isomers okay. So that is why we say that it is existing as a non-resolvable dl-pair.

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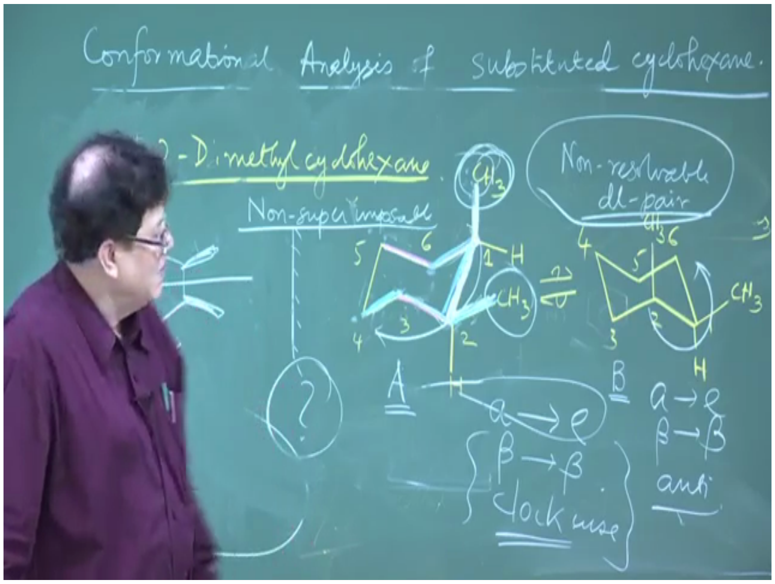

If you go by the planar conformation that is the hexagon. this type of conclusion you cannot fetch (())(24:19), because planar conformations is that it is a mesopher (())(24:23) that it is a mesopher form, because it has got a (())(24:27) but that is not corrected it is not a mesopher, see initially people try to measure the optical activity the rotation, but they never got the rotation out of this. So they thought then meso is alright that they are saying it is meso, meso means no optical activity, but that is wrong. This is not meso, it is non-resolvable dl-pair, the reason it does not show any optical activity, because you cannot separate these two may be at very low temperature it is possible and one day we will come when people will isolate these at very low temperature isomer (())(25:02) okay, but the question is basically we are talking about the room temperature chemistry that at room temperature under ambient condition what happens we cannot separate it. They exist at the non-resolvable dl-pair okay that is for the Cis compound okay.

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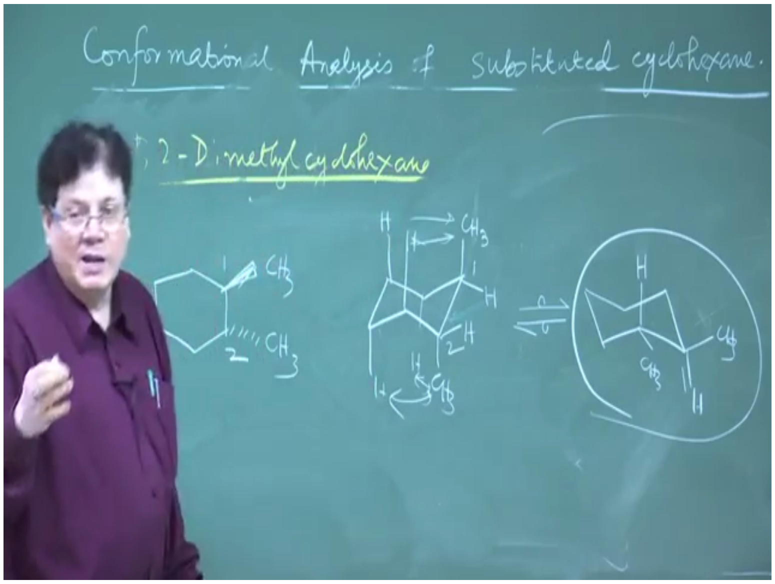

For the trans compound again I first draw the planar formula, this is the trans one, so if you write in the cyclohexane chair form, suppose this is the one carbon, this is the 2 and C1 because it is beta, so we have to put the methyl in the axial position and we have to put the other methyl alpha that also in the axial position. So this is one form if you flip it you get the mirror image chair, but you gain something and what is that.

Now both the methyls see this is the number 1 methyl 2, so 1 is here now. So methyl is here and the2 methyl is here. So both the methyls are now occupying equatorial position. So it is a di-equatorial system and this is a diaxial system. So it will be mostly almost 100 percent close to 100 percent (())(26:48) hydrogen form. Why, because we can say that the rule of thumb that the groups do not occupy the axial position, because there is 1,3-diaxail interaction. So when you put the methyl in a axial position so you have how many diaxial interactions here and then one is for this up methyl and the other is for the down methyl that is one way of explaining the instability of this, because it suffers from this 2 here 4 interactions methyl hydrogen diaxial interaction, which is not present here, okay.

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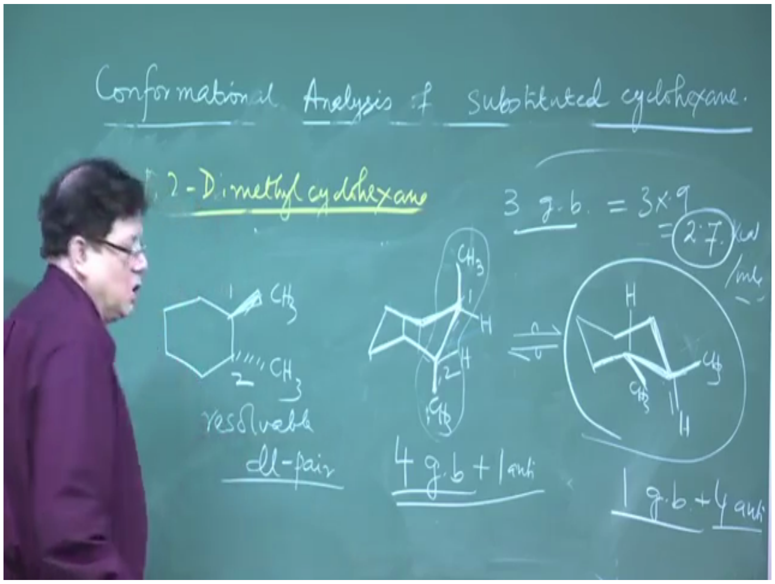

The other way you can again start calculating the number of extra butane units that you incorporate and what is their status okay? What is their status okay and see extra butane units will be again why, because for each carbon you are introducing the two butane units and then there mutual relationship that also constitutes one more butane unit that we have seen in the Cis form. So now what is the energy difference between this and that? In the Cis form there was no energy difference, because one was axial another equatorial. Here this is diaxial this is di-equatorial. So what is the energy difference between the two? So that will rely on the butane units what is the status of the butane units. So this is axial, so that will immediately put to gauche butane units. This is also axial that will immediately put 2 butane units to gauche butane units okay.

So these two axial methyl have 4 gauche butane units interactions and the mutual one interestingly fortunately the mutual once are in the anti-form. So the other one is anti (())(28:50). In the case of Cis form in the sorry, in the case of di-equatorial form this is equatorial, so that extra butane units these are all anti. So this is the anti for the equatorial methyls you do not have we have all anti, but the mutual one the question is what happens to the mutual, I can show you what happens to the mutual once, see this is the diaxial form this is axial that is axial and what is the di-equatorial form that you flip it take this up and take this down. So this is the di-equatorial form this is equatorial that is equatorial. What is a relationship between these di-equatorial?

So look at these the dihedral angle the 60 degree, so the mutual butane unit is it is (())(29:44) having a 60 degree dihedral angle. So that constitutes 1 gauche unit okay plus 4 anti and that is due to the incorporation of equatorial form that is the normal. The mutual one is the gauche, so the difference in energy between these two is what will be 3 gauche butane interactions that means 3 into 9 (())(30:16) and that is the correct way of (())(30:24) see if you look at the, so we are calculating on the basis of this 1,3-diaxail interaction and we landed up having 4, but here if you do it correctly as the butane units, so ultimately the difference comes to be 2.7. So ultimately the difference comes to be 2.7 (())(30:42), okay and regarding optical activity.

Now there is this flipping is almost stop, because this is not present, so you have only this and you can draw the mirror image the way I said you can draw the mirror image and the mirror image will not be identical the mirror image is non-superimposable and in this case flipping does not give you the mirror image. So it will represent again resolvable dl-pair it will be present as a resolvable dl-pair, I think next day we will start turning this molecules and what is the perspective projection formula to turn it to 60 degree then 120 degree and the where are the positions (())(31:33), but that way that is the very basic (())(31:38) to compare between two cyclohexane rings okay.

The way I did it, is a kind of mnemonic device just to help you out in sorting out this type form that we have i(())(31:52) alpha beta nature and the axial equatorial nature okay. So the that part we do the next time (())(31:58) and we will also cover the 1,3 and 1,4 disubstituted systems thank you.